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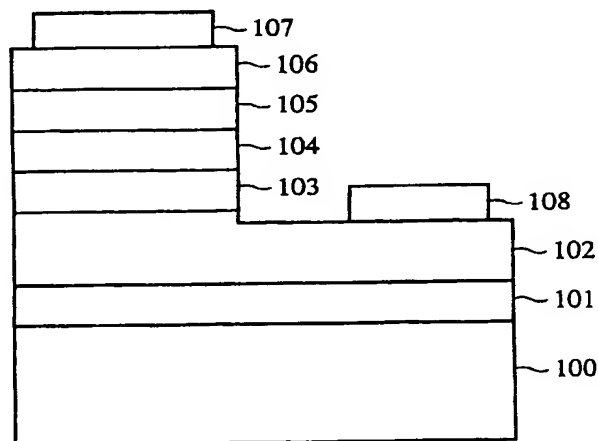
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(54) **BLUE LIGHT EMITTING DEVICE AND PRODUCTION METHOD THEREOF**

(57) A gallium-nitride-based blue light emitting element that is manufacturable through a small number of processes and a method of manufacturing the same are disclosed. A first gallium-nitride-based semiconductor layer containing impurities of a first conductivity type, a gallium-nitride-based semiconductor active layer that is substantially intrinsic, and a second gallium-nitride-based semiconductor layer containing impurities of a second conductivity type that is opposite to the first conductivity type are formed according to a thermal CVD method and are left in an inert gas to cool by themselves.

**FIG.1**



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## Description

### Technical Field

The present invention relates to a blue light emitting element employing a gallium-nitride-based compound semiconductor and a method of manufacturing the same.

### Background Art

Gallium-nitride-based compound semiconductors such as GaN, InGaN, and GaAlN are drawing attention as materials for fabricating blue light emitting diodes (LEDs) and blue laser diodes (LDs). This kind of compound semiconductor is capable of emitting blue light of an intensity seldom achieved before.

A blue light emitting element employing a gallium-nitride-based compound semiconductor is disclosed in, for example, Japanese Unexamined Patent Publication No. 4-321280. Figure 7 shows the basic structure of a blue light emitting element 2 according to a prior art. On a sapphire substrate 200, a buffer layer 201 is formed. On the buffer layer 201, an n-type GaN semiconductor layer 202 and a p-type GaN semiconductor layer 203 are formed. Between the layers 202 and 203, there is a depletion layer to which carriers are injected to emit light.

The blue light emitting element is manufactured by growing crystals on a sapphire substrate according to a CVD method and by forming gallium nitride semiconductor layers on the substrate. The substrate is properly cut into chips. Each chip is connected to a wire frame, and wiring is made to complete a device.

A natural cooling process in an inert gas is disclosed in Japanese Unexamined Patent Publication No. 8-125222. To replace an atmospheric gas at room temperature with an inert gas, according to this disclosure, a reactive tube is evacuated under a high temperature. This high temperature may grow a substrate. When evacuating the reactive tube, the grown crystals may evaporate. As a result, no grown crystals may be left, or the crystallized film may be thinned.

In the gallium-nitride-based blue light emitting element of the prior art, impurities in the semiconductor layers are not sufficiently activated. Accordingly, the prior art needs an after-treatment of thermal annealing.

The thermal annealing increases the number of processes and processing time. Since the gallium nitride semiconductor is exposed to a high temperature of 600°C or more for a long time, nitrogen may escape from crystals and deteriorate surface homology. This results in changing semiconductor properties and deteriorating blue light emitting efficiency and yield.

### Disclosure of Invention

An object of the present invention is to provide a gallium-nitride-based blue light emitting element involv-

ing a small number of manufacturing processes, and a method of manufacturing the same.

Another object of the present invention is to provide a gallium-nitride-based blue light emitting element realizing high yield, and a method of manufacturing the same.

Still another object of the present invention is to provide a gallium-nitride-based blue light emitting element proper for mass-production, and a method of manufacturing the same.

Still another object of the present invention is to provide a gallium-nitride-based blue light emitting element realizing high-intensity light and low power consumption, and a method of manufacturing the same.

In order to accomplish these objects, the present invention provides a blue light emitting element consisting of a first gallium-nitride-based semiconductor layer containing impurities of a first conductivity type, a gallium-nitride-based semiconductor active layer that is substantially intrinsic, and a second gallium-nitride-based semiconductor layer containing impurities of a second conductivity type that is opposite to the first conductivity type. The first and second gallium-nitride-based semiconductor layers and gallium-nitride-based semiconductor active layer are formed according to a thermal CVD method and are left in an inert gas to cool by themselves, so that seven percent or more of the impurities are activated.

The present invention also provides a method of manufacturing a blue light emitting element including the steps of forming, according to a thermal CVD method in a vacuum chamber, a first gallium-nitride-based semiconductor layer containing impurities of a first conductivity type, a gallium-nitride-based semiconductor active layer that is substantially intrinsic, and a second gallium-nitride-based semiconductor layer containing impurities of a second conductivity type that is opposite to the first conductivity type, and leaving the layers in an inert gas so that the layers may cool by themselves.

The present invention involves simple processes without thermal annealing and improves yield. The gallium-nitride-based compound semiconductor blue light emitting element of the present invention produces high-intensity light with small power consumption.

### Brief Description of Drawings

Figure 1 is a sectional view showing the structure of a gallium-nitride-based compound semiconductor blue light emitting diode chip according to the present invention;

Fig. 2 is a schematic view showing a CVD apparatus for forming a gallium-nitride-based compound semiconductor blue light emitting diode chip according to the present invention;

Fig. 3 is a graph showing temperature changes when manufacturing a gallium-nitride-based compound semiconductor blue light emitting diode

according to the present invention;

Fig. 4 shows a gallium-nitride-based compound semiconductor blue light emitting diode according to another embodiment of the present invention;

Fig. 5 shows a gallium-nitride-based compound semiconductor blue light emitting diode employing a semiconductor laser according to the present invention;

Fig. 6 shows another gallium-nitride-based semiconductor blue light emitting diode employing a semiconductor laser according to the present invention; and

Fig. 7 is a sectional view showing the structure of a gallium-nitride-based compound semiconductor blue light emitting diode chip according to a prior art.

### Best Mode for Carrying Out the Invention

A method of manufacturing a gallium-nitride-based compound semiconductor blue light emitting diode according to the present invention will be explained with reference to Fig. 1.

The gallium-nitride-based compound semiconductor blue light emitting diode 1 has a sapphire substrate 100. On the substrate 100, a gallium-nitride-based semiconductor buffer layer 101 and a gallium-nitride-based n-type semiconductor contact layer 102 are formed. On the layer 102, a gallium-nitride-based n-type semiconductor clad layer 103, a gallium-nitride-based semiconductor active layer 104, a gallium-nitride-based p-type semiconductor clad layer 105, and a gallium-nitride-based p-type semiconductor contact layer 106 are formed. An electrode 108 is formed in contact with the layer 102. An electrode 107 is formed in contact with the layer 105.

The present invention employs  $\text{InAlGa}\text{N}$  compound semiconductor as the gallium-nitride-based semiconductor. This semiconductor is capable of emitting a wide range of blue light by adjusting the composition thereof. Examples of compositions will be explained. The composition of  $\text{In}_x\text{Al}_y\text{Ga}_{(1-x-y)}\text{N}$ , where  $0 \leq x \leq 1$ ,  $0 \leq y \leq 1$ , and  $x + y \leq 1$ .

The gallium-nitride-based n-type semiconductor buffer layer 101 relaxes lattice mismatch between the gallium-nitride-based semiconductor contact layer 102 and the sapphire substrate 100. Values for the parameters of  $\text{In}_x\text{Al}_y\text{Ga}_{(1-x-y)}\text{N}$  are, for example,  $0 \leq x \leq 1$  and  $0 \leq y \leq 1$ , preferably,  $0 \leq x \leq 0.5$  and  $0 \leq y \leq 0.5$ .

The gallium-nitride-based n-type semiconductor contact layer 102 serves as a contact surface for the electrode 108. Values for the parameters of  $\text{In}_x\text{Al}_y\text{Ga}_{(1-x-y)}\text{N}$  for the layer 102 are, for example,  $0 \leq x \leq 1$  and  $0 \leq y \leq 1$ , preferably,  $0 \leq x \leq 0.3$  and  $0 \leq y \leq 0.3$ . To make the layer be of n-type, impurities such as silicon and selenium are added thereto at an impurity concentration of  $6 \times 10^{18} \text{ cm}^{-3}$ .

The gallium-nitride-based n-type semiconductor

clad layer 103 forms the n side of a pin junction that forms a light emitting region. Values for the parameters of  $\text{In}_x\text{Al}_y\text{Ga}_{(1-x-y)}\text{N}$  are properly adjusted according to a required wavelength of light and are, for example,  $0 \leq x \leq 1$  and  $0 \leq y \leq 1$ , preferably,  $0 \leq x \leq 0.3$  and  $0.1 \leq y \leq 1$ . To make the layer be of n-type, impurities such as silicon and selenium are added thereto at an impurity concentration of  $3 \times 10^{18} \text{ cm}^{-3}$ .

The gallium-nitride-based semiconductor active layer 104 is substantially an intrinsic semiconductor layer that forms a main part of the light emitting region. Values for the parameters of  $\text{In}_x\text{Al}_y\text{Ga}_{(1-x-y)}\text{N}$  are properly adjusted according to a required wavelength of light and are, for example,  $0 \leq x \leq 1$  and  $0 \leq y \leq 1$ , preferably,  $0 \leq x \leq 0.6$  and  $0 \leq y \leq 0.5$ .

The gallium-nitride-based p-type semiconductor clad layer 105 forms the p side of the pin junction that forms the light emitting region. Values for the parameters of  $\text{In}_x\text{Al}_y\text{Ga}_{(1-x-y)}\text{N}$  are properly adjusted according to a required wavelength of light and the gallium-nitride-based n-type semiconductor clad layer 103 and gallium-nitride-based semiconductor active layer 104 and are, for example,  $0 \leq x \leq 1$  and  $0 \leq y \leq 1$ , preferably,  $0 \leq x \leq 0.3$  and  $0.1 \leq y \leq 1.0$ . To make the layer be of p-type, impurities such as magnesium, beryllium, and zinc are added thereto at an impurity concentration of  $3 \times 10^{18} \text{ cm}^{-3}$ .

The gallium-nitride-based p-type semiconductor contact layer 106 serves a contact surface for the electrode 107. Values for the parameters of  $\text{In}_x\text{Al}_y\text{Ga}_{(1-x-y)}\text{N}$  are, for example,  $0 \leq x \leq 1$  and  $0 \leq y \leq 1$ , preferably,  $0 \leq x \leq 0.3$  and  $0 \leq y \leq 0.3$ . To make the layer be of p-type, impurities such as magnesium, beryllium, and zinc are added thereto at an impurity concentration of  $8 \times 10^{18} \text{ cm}^{-3}$ .

The electrode 107 is a transparent electrode with respect to the gallium-nitride-based semiconductor active layer 104. More precisely, it is a compound of metal such as ITO (indium tin oxide) and oxygen, or it may be a very thin film of metal such as Al and Ni.

The other electrode 108 is not necessarily transparent. It may be made of metal such as Ti, Al, and Ni.

The values mentioned above for the parameters of  $\text{In}_x\text{Al}_y\text{Ga}_{(1-x-y)}\text{N}$  are set so that the band gap of each of the gallium-nitride-based n-type semiconductor clad layer 103 and gallium-nitride-based p-type semiconductor clad layer 105 is larger than that of the gallium-nitride-based semiconductor active layer 104. This results in an increase in the number of carriers that are injected into the layer 104, to further improve the intensity of emitted light.

These gallium-nitride-based semiconductor layers are formed on the sapphire substrate according to, for example, the thermal CVD method. Figure 2 shows a CVD apparatus. This apparatus has a vacuum chamber 20, a substrate holder 21 disposed in the chamber, a reactive gas introducing pipe 22, an evacuation pipe 23, and a high-frequency coil (not shown) for heating a substrate set on the holder 21.

At first, a sapphire substrate 100 is set on the substrate holder 21. The vacuum chamber 20 is evacuated from 760 to 1 Torr. Then, high-frequency heating is started, and a reactive gas containing organic metal is introduced. The reactive gas may contain Ga(CH<sub>3</sub>)<sub>3</sub>, In(CH<sub>3</sub>)<sub>3</sub>, Al(CH<sub>3</sub>)<sub>3</sub>, and NH<sub>3</sub> and is introduced with a carrier gas containing hydrogen and nitrogen. A reaction pressure is about 760 Torr.

In this way, gallium-nitride-based semiconductor material is formed. The composition of the reactive gas is properly changed to adjust the composition of each layer as desired. Impurities are added by properly introducing SiH<sub>4</sub> and Cp<sub>2</sub>Mg.

Figure 3 shows temperature changes in the vacuum chamber 20 when forming the gallium-nitride-based semiconductor. The temperature of the substrate is increased to within the range 1000°C to 1400°C (inclusive), for example to 1200°C, to form a gallium-nitride-based semiconductor buffer layer. The temperature is dropped by an amount of from 50°C to 200°C, down to a temperature of 800°C to 1200°C. For example, the temperature is dropped from 1200°C to 1100°C to form a n-type contact layer and an n-type clad layer by adding proper impurities. To form an active layer, the temperature is dropped by a amount of from 300°C to 600°C. For example, the temperature is dropped from 1100°C to a temperature in the range 900°C to 600°C (inclusive). Lastly, the temperature of the substrate is increased to the first temperature, for example, 1100°C to form a p-type clad layer and a p-type contact layer, thereby completing the element.

The present invention completely replaces the reactive gas in the vacuum chamber 20 with an inert gas. The inert gas is preferably nitrogen, or may be He or Ar.

After the vacuum chamber 20 is filled with the inert gas, the pressure of the chamber is adjusted to 600 to 900 Torr, for example, 760 Torr. This state is maintained for two to three hours. Then, the temperature of the substrate drops to room temperature, for example, 25°C. The sapphire substrate is removed from the vacuum chamber 20.

The sapphire substrate removed from the vacuum chamber 20 is properly cut by diamond cutter into many chips. Each chip forms a blue light emitting element that emits light having sufficient intensity. Accordingly, there is no need for a thermal annealing after-treatment.

Since there is no need to carry out the thermal annealing after-treatment on the sapphire substrate taken out of the vacuum chamber 20, the present invention simplifies manufacturing processes and shortens the manufacturing time. The intensity of light emitted from the produced element is higher than that of the prior art.

The reason for this will be explained. The prior art activates impurities by thermal annealing. Actual measurements on prior art devices show, however, that only about one percent of the impurities are activated. The remaining 99 percent is not only useless but also inter-

fering because it causes lattice defects to act as carrier traps. Namely, injected carriers are mostly trapped thereby and do not work to emit light.

On the other hand, actual measurements on the present invention show that seven percent or more, usually about 10 percent of injected carriers are activated. In this way, the present invention activates many carriers and reduces resistance, to drop power consumption.

Figure 4 is a sectional view showing the structure of a light emitting diode 500 according to another embodiment of the present invention. A method of manufacturing the light emitting diode 500 will be explained with reference to the figure.

A sapphire substrate 501 having a plane c as a principal plane is cleaned for organic and acid matter. The substrate is set on a susceptor to be heated in an MOCVD apparatus. Heating is carried out by a resistive or inductive heater.

Oxygen is supplied to the sapphire substrate 501 at a rate of 10 L/min, and the substrate is heat-treated at 1100°C for about 10 minutes to remove process damage and oxides from the surface thereof.

The temperature is dropped to 550°C, and hydrogen at 15 L/min, nitrogen at 5 L/min, ammonia at 10 L/min, and TMG (trimethyl gallium) at 25 cc/min are supplied for four minutes to form a GaN buffer layer 502 of 30 nm thick.

The TMG is stopped, and the temperature is increased up to 1100°C at a speed of 50°C/min or slower. If the rate of temperature increase is faster than 50°C per minute, the surface of the buffer layer 502 will be roughened to form irregularities on the surface of a monocrystalline layer.

The temperature is kept at 1100°C, and hydrogen at 15 L/min, nitrogen at 5 L/min, ammonia at 10 L/min, and TMG at 100 cc/min are supplied to form a gallium-nitride-based monocrystalline semiconductor (GaN) buffer layer 503 of 1.8 μm thick.

The temperature is kept at 1100°C, and a silane gas is added at 10 cc/min for 130 minutes to the material gas, to form an n-type GaN contact injection layer 504 of 4 μm thick.

The TMG, silane gas, and hydrogen are stopped, and the temperature is dropped down to 780 °C.

The temperature is kept at 780°C, and nitrogen at 20 L/min, hydrogen at 100 cc/min, ammonia at 10 L/min, TMG at 12 cc/min, TMI (trimethyl indium) at 150 cc/min, silane gas at 3 cc/min, and DMZ (dimethyl zinc) at 20 cc/min are supplied for six minutes to form an InGaN semiconductor active layer 505 of 0.2 μm thick serving as a light emitting layer.

Nitrogen at 20 L/min, hydrogen at 100 cc/min, and ammonia at 10 L/min are supplied, and the temperature is increased up to 1100°C.

The temperature is kept at 1100°C, and nitrogen at 20 L/min, hydrogen at 150 cc/min, ammonia at 10 L/min, TMG at 100 cc/min, and Cp<sub>2</sub>Mg (cyclopentadienyl magnesium) at 50 cc/min are supplied for 10 min-

utes to form a p-type GaN contact injection layer 506 of 0.3  $\mu\text{m}$  thick.

Although the p-type layer is single in this embodiment, it is possible to separately form a contact layer and an injection layer. In this case, the contact layer is made from GaN and the injection layer from AlGaIn so that the contact layer may have a higher carrier concentration than the injection layer.

The supplied gas is switched to nitrogen at 30 L/min, and the temperature is dropped to room temperature. As a result, the p-type GaN layer shows an activation ratio of 8% with respect to an Mg concentration of  $3 \times 10^{19} \text{ cm}^{-3}$ . The activation ratio is obtained by standardizing an acceptor concentration according to an Mg concentration. If the temperature is dropped to 400°C with nitrogen at 20 L/min and ammonia at 10 L/min, and from 400°C to room temperature with only nitrogen at 30 L/min, an activation ratio of 7% or greater is secured.

Generally, gallium-nitride-based semiconductor has the problem of denitrification. To prevent the problem, a compound that produces nitrogen ions instead of nitrogen itself is effective. This is the reason why ammonia is used in addition to nitrogen. If the ammonia is too much, hydrogen will reversely affect strongly. According to experiments, a preferable ratio of nitrogen to ammonia is 2:1.

The layer structure thus formed is heat-treated at 750°C for one minute to further increase the carrier concentration in the p-type layer 506 and realize p-type crystals of  $2 \times 10^{17} \text{ cm}^{-3}$ .

The layer structure is patterned with the use of, for example,  $\text{SiO}_2$  and is etched according to a reactive ion etching (RIE) method using  $\text{Cl}_2$  and  $\text{BCl}_3$  to expose a part of the n-type GaN layer 504.

An electrode for the p-type layer 506 is formed by depositing Ni for 20 nm and gold for 400 nm (510 in Fig. 4) according to a known vacuum deposition method and sputtering method. An electrode for the n-type layer 504 is formed by depositing Ti for 20 nm and gold for 400 nm (511 in Fig. 4). The electrode for the p-type layer may be not only the laminated structure of Ni/Au but also a monolayer of Pd, Ti, Pt, or In, a laminated structure thereof with Ni and Au, or an alloy thereof. The electrode for the n-type layer may be made of Ti and Au, a monolayer of Al or In, a laminated structure including Ti and Au, or an alloy thereof.

On the p-type electrode 510, a protection film of  $\text{SiO}_2$  is formed, to complete the element.

Although the embodiment relates to a light emitting diode, the gist of the present invention is the method of manufacturing a p-type layer. Accordingly, the present invention is applicable to a semiconductor laser employing GaN-based semiconductor.

Figure 5 shows the structure of a blue light emitting element employing such a semiconductor laser.

On a sapphire substrate 701, there are formed a gallium-nitride-based semiconductor buffer layer 702, a gallium-nitride-based n-type semiconductor contact layer 703, a gallium-nitride-based n-type semiconductor

layer 704, a gallium-nitride-based n-type semiconductor clad layer 705, a gallium-nitride-based semiconductor active layer 706, a gallium-nitride-based p-type semiconductor clad layer 707, a gallium-nitride-based p-type semiconductor layer 708, a gallium-nitride-based p-type semiconductor layer 709, and a gallium-nitride-based p-type semiconductor contact layer 710.

Similar to the embodiment of Fig. 4, a part of the structure is etched according to the reactive ion etching method to partly expose the surface of the gallium-nitride-based n-type semiconductor contact layer 703. On the exposed surface, Ti, Au, Ti, and Au are laminated in this order to form an n-type electrode. The thicknesses thereof are 200  $\mu\text{m}$ , 4000 angstroms, 200  $\mu\text{m}$ , and 1  $\mu\text{m}$ , respectively. A p-type electrode 711 may be formed by laminating Pd, Ti, Pt, and Ti in this order. The thicknesses thereof are 200  $\mu\text{m}$ , 4000 angstroms, 200  $\mu\text{m}$ , and 1  $\mu\text{m}$ , respectively.

The gallium-nitride-based semiconductor active layer 706 is made of  $\text{In}_x\text{Ga}_{(1-x)}\text{N}$  compound semiconductor having a quantum well structure. The layer is made by alternately laminating a film of 25 angstroms thick with  $x = 0.05$  and  $y = 0.95$  and a film of 25 angstroms thick with  $x = 0.20$  and  $y = 0.80$  about 20 times, to form a multilayer quantum well.

Any other gallium-nitride-based semiconductor layer is basically made of GaN. Examples of thicknesses are 70  $\mu\text{m}$  for the sapphire substrate 701, 500 angstroms for the gallium-nitride-based semiconductor buffer layer 702, 4  $\mu\text{m}$  for the gallium-nitride-based n-type semiconductor contact layer 703, 0.3  $\mu\text{m}$  for the gallium-nitride-based n-type semiconductor layer 704, 0.2  $\mu\text{m}$  for the gallium-nitride-based n-type semiconductor clad layer 705, 0.2  $\mu\text{m}$  for the gallium-nitride-based p-type semiconductor clad layer 707, 0.3  $\mu\text{m}$  for the gallium-nitride-based p-type semiconductor layer 708, 0.9  $\mu\text{m}$  for the gallium-nitride-based p-type semiconductor layer 709, and 0.1  $\mu\text{m}$  for the gallium-nitride-based p-type semiconductor contact layer 710.

Examples for impurity concentrations are  $2 \times 10^{18} \text{ cm}^{-3}$  for the gallium-nitride-based n-type semiconductor contact layer 703,  $5 \times 10^{17} \text{ cm}^{-3}$  for the gallium-nitride-based n-type semiconductor layer 704,  $5 \times 10^{17} \text{ cm}^{-3}$  for the gallium-nitride-based n-type semiconductor clad layer 705,  $5 \times 10^{17} \text{ cm}^{-3}$  for the gallium-nitride-based p-type semiconductor clad layer 707,  $5 \times 10^{17} \text{ cm}^{-3}$  for the gallium-nitride-based p-type semiconductor layer 708,  $3 \times 10^{18} \text{ cm}^{-3}$  for the gallium-nitride-based p-type semiconductor layer 709, and  $2 \times 10^{19} \text{ cm}^{-3}$  for the gallium-nitride-based p-type semiconductor contact layer 710.

After the gallium-nitride-based p-type semiconductor layer 708 is formed, the reactive ion etching method may be used to etch up to the gallium-nitride-based n-type semiconductor contact layer 703. The etched part is filled with a GaN layer of high resistance with Zn, to limit a resonance part. An example of this kind of structure is shown in Fig. 6. A high-resistance GaN layer 800 contains Zn of  $2 \times 10^{18} \text{ cm}^{-3}$  in concentration.

## Industrial Applicability

As explained above, the present invention provides a gallium-nitride-based compound semiconductor blue light emitting element that is manufactured through simple processes at high yield.

The gallium-nitride-based compound semiconductor blue light emitting element of the present invention provides high-intensity light at low power consumption.

## Claims

1. A blue light emitting element comprising a first gallium-nitride-based semiconductor layer containing impurities of a first conductivity type, a gallium-nitride-based semiconductor active layer that is substantially intrinsic, and a second gallium-nitride-based semiconductor layer containing impurities of a second conductivity type that is opposite to the first conductivity type, the first and second gallium-nitride-based semiconductor layers and gallium-nitride-based semiconductor active layer are formed according to a thermal CVD method and are left in an inert gas to cool by themselves, so that seven percent or over of the impurities are activated.
2. The blue light emitting element of claim 1, wherein the first and second gallium-nitride-based semiconductor layers and gallium-nitride-based semiconductor active layer are formed on a sapphire substrate.
3. The blue light emitting element of claim 1, wherein a gallium-nitride-based semiconductor buffer layer of the first conductivity type is formed between the sapphire substrate and the first gallium-nitride-based semiconductor layer.
4. A method of manufacturing a blue light emitting element, comprising the steps of forming, in a vacuum chamber, a first gallium-nitride-based semiconductor layer containing impurities of a first conductivity type, a gallium-nitride-based semiconductor active layer that is substantially intrinsic, and a second gallium-nitride-based semiconductor layer containing impurities of a second conductivity type that is opposite to the first conductivity type, and leaving the layers in an inert gas so that the layers may cool by themselves.
5. A method of manufacturing a blue light emitting element, comprising the steps of inserting a substrate into a vacuum chamber, heating the substrate up to 1000°C to 1400°C to form a gallium-nitride-based semiconductor buffer layer, decreasing the substrate temperature by 50°C to 200°C to form an n-type contact layer and an n-type clad layer each made of gallium-nitride-based semiconductor containing impurities, further decreasing the substrate temperature by 300°C to 600°C to form a gallium-nitride-based semiconductor active layer, heating the substrate 1000°C to 1400°C to form a p-type clad layer and a p-type contact layer, replacing a reactive gas in the vacuum chamber with an inert gas, adjusting an internal pressure of the vacuum chamber to 600 to 900 Torr, for example, 760 Torr, and leaving the vacuum chamber as it is for two to three hours to cool the substrate by itself down to room temperature.
6. The method of manufacturing a blue light emitting element, wherein the inert gas is of nitrogen, He or Ar.
7. A method of manufacturing a blue light emitting element having a sapphire substrate, a GaN buffer layer, an  $\text{In}_x\text{Al}_y\text{Ga}_z\text{N}$  ( $x + y + z \leq 1$ ,  $0 \leq x \leq 1$ ,  $0 \leq y \leq 1$ ,  $0 \leq z \leq 1$ ) semiconductor layer having a first conductivity type, an  $\text{In}_x\text{Al}_y\text{Ga}_z\text{N}$  ( $x + y + z \leq 1$ ,  $0 \leq x \leq 1$ ,  $0 \leq y \leq 1$ ,  $0 \leq z \leq 1$ ), semiconductor active layer having the first conductivity type, and an  $\text{In}_x\text{Al}_y\text{Ga}_z\text{N}$  ( $x + y + z \leq 1$ ,  $0 \leq x \leq 1$ ,  $0 \leq y \leq 1$ ,  $0 \leq z \leq 1$ ) semiconductor layer having a second conductivity type, comprising the step of forming a p-type  $\text{In}_x\text{Al}_y\text{Ga}_z\text{N}$  ( $x + y + z \leq 1$ ,  $0 \leq x \leq 1$ ,  $0 \leq y \leq 1$ ,  $0 \leq z \leq 1$ ) semiconductor layer through a growing process that employs a carrier gas substantially made of an inert gas and a material gas containing an organic metal gas and an ammonia gas, and a process of leaving the formed structure in an inert gas to cool by itself just after the growing process.
8. The method of manufacturing a blue light emitting element of claim 7, wherein the activation ratio of p-type impurities is 7% or greater.
9. A method of manufacturing a blue light emitting element having a sapphire substrate, an  $\text{Al}_a\text{Ga}_b\text{N}$  ( $a + b \leq 1$ ,  $0 \leq a \leq 1$ ) buffer layer, an  $\text{In}_x\text{Al}_y\text{Ga}_z\text{N}$  ( $x + y + z \leq 1$ ,  $0 \leq x \leq 1$ ,  $0 \leq y \leq 1$ ,  $0 \leq z \leq 1$ ) semiconductor layer having a first conductivity type, an  $\text{In}_x\text{Al}_y\text{Ga}_z\text{N}$  ( $x + y + z \leq 1$ ,  $0 \leq x \leq 1$ ,  $0 \leq y \leq 1$ ,  $0 \leq z \leq 1$ ) semiconductor active layer having the first conductivity type, and an  $\text{In}_x\text{Al}_y\text{Ga}_z\text{N}$  ( $x + y + z \leq 1$ ,  $0 \leq x \leq 1$ ,  $0 \leq y \leq 1$ ,  $0 \leq z \leq 1$ ) semiconductor layer having a second conductivity type, comprising the step of forming a p-type  $\text{In}_x\text{Al}_y\text{Ga}_z\text{N}$  ( $x + y + z \leq 1$ ,  $0 \leq x \leq 1$ ,  $0 \leq y \leq 1$ ,  $0 \leq z \leq 1$ ) semiconductor layer through a growing process that employs a carrier gas substantially made of an inert gas and a material gas containing an organic metal gas and an ammonia gas, a process of leaving the formed structure in an inert gas to cool by itself just after the growing process, and a process of heat-treating, at a temperature of 400°C or higher, the formed structure that has been cooled to room temperature.
10. The method of manufacturing a blue light emitting

element of claim 7, wherein an ammonia gas is introduced during a part of the natural cooling process.

11. The method of manufacturing a blue light emitting  
element of claim 10, wherein a part of the natural  
cooling process is carried out between a growth  
temperature and 350°C to 600°C.

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FIG.1

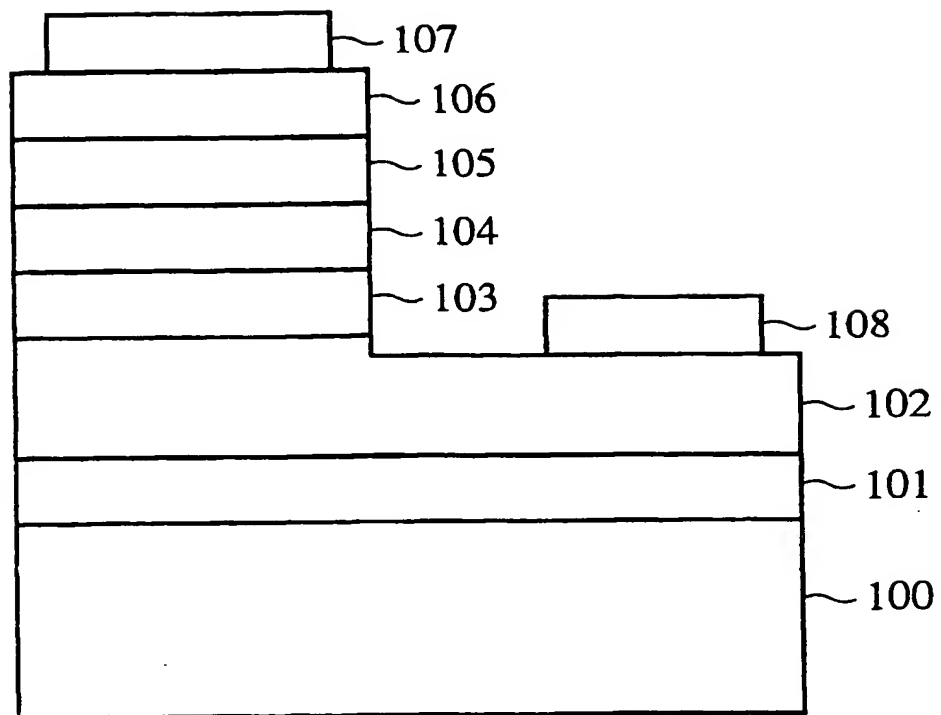




FIG.2

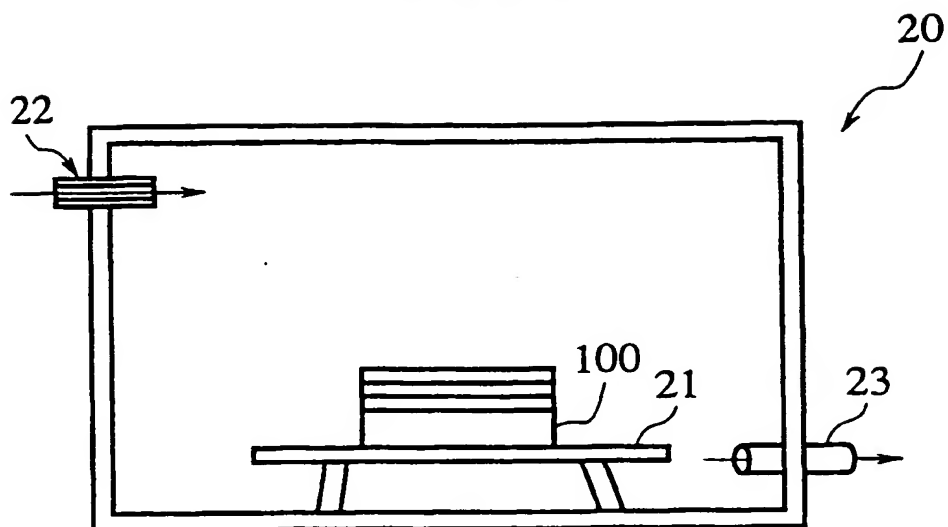


FIG.3

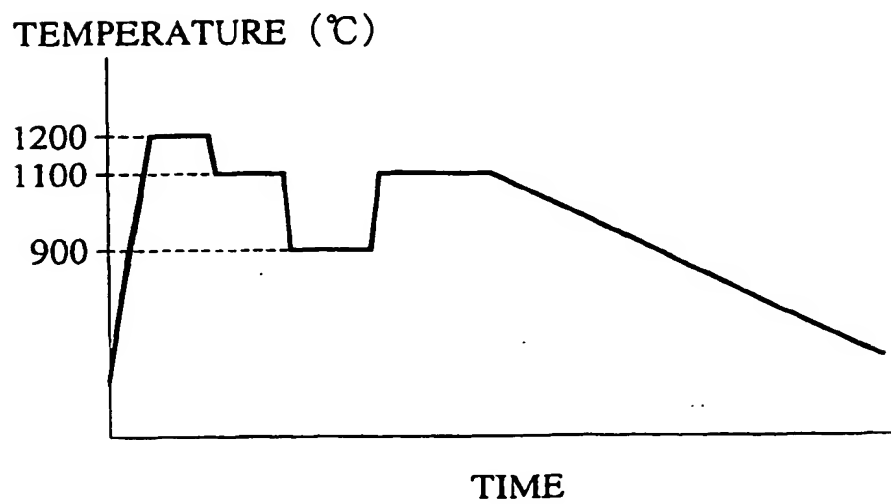


FIG.4

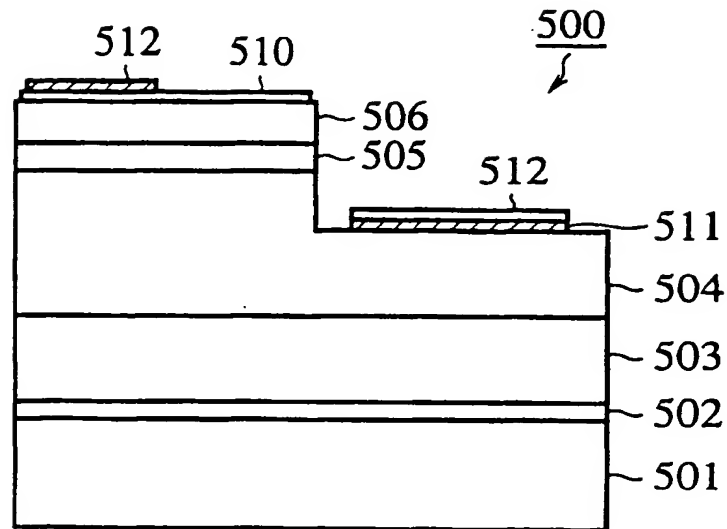


FIG.5

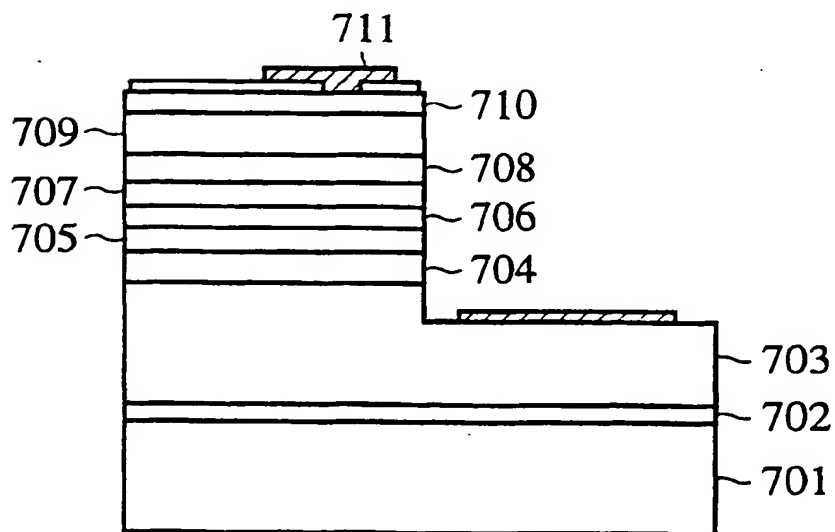


FIG.6

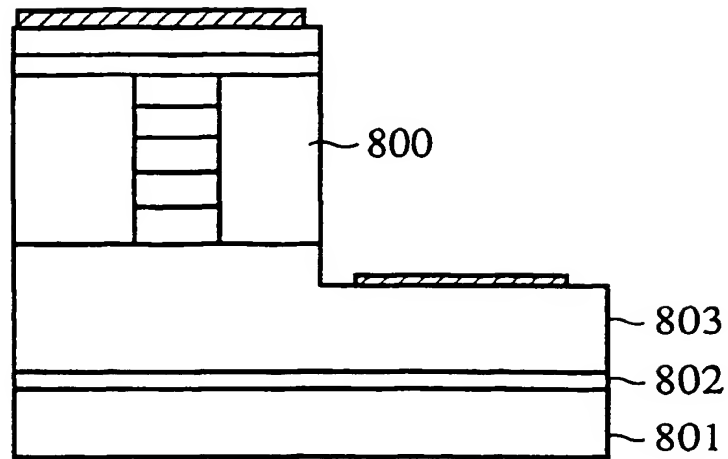
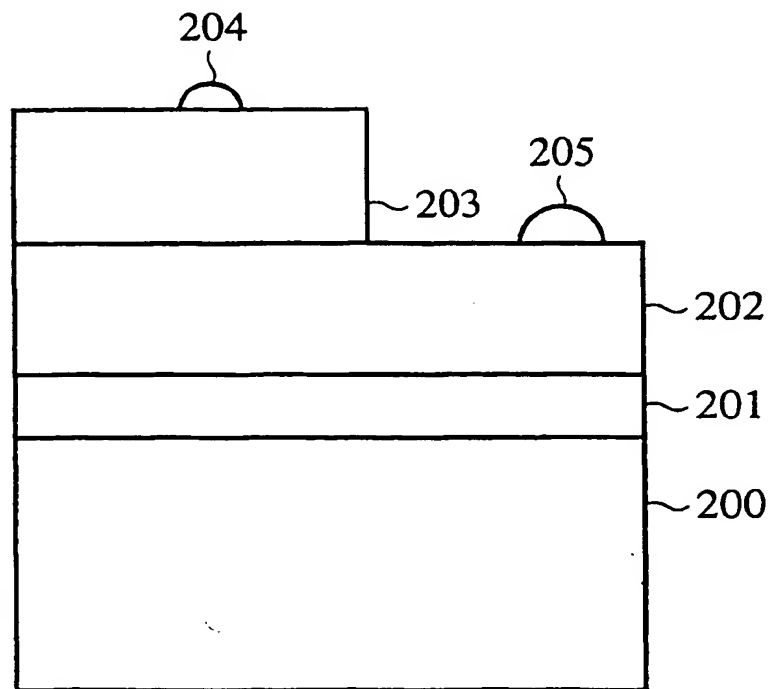


FIG.7



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP96/02434

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> Int. Cl <sup>6</sup> H01L33/00 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) Int. Cl <sup>6</sup> H01L33/00, H01S3/18 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1965 - 1996 Kokai Jitsuyo Shinan Koho 1971 - 1996 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P	JP, 8-8460, A (Mitsubishi Cable Industries, Ltd.), January 12, 1996 (12. 01. 96), Page 4, left column, lines 40 to 41 (Family: none)	1
P	JP, 8-32113, A (Mitsubishi Cable Industries, Ltd.), February 2, 1996 (02. 02. 96), Page 2, left column, lines 2 to 6 (Family: none)	1 - 4
A	JP, 6-232451, A (Nichia Chemical K.K.), August 19, 1994 (19. 08. 94), Page 2, left column, lines 2 to 8 (Family: none)	1
A	JP, 6-196755, A (Nichia Chemical K.K.), July 15, 1994 (15. 07. 94), Page 4, right column, lines 14 to 16 (Family: none)	1
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family		
Date of the actual completion of the international search November 19, 1996 (19. 11. 96)		Date of mailing of the international search report December 3, 1996 (03. 12. 96)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.		Authorized officer Telephone No.

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